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ORIGINAL ARTICLE

Mixed ligand complexes of $[Pd(terpy)(H_2O)]^{2+}$ with some selected amino acids, peptides, DNA and related ligands

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DNA

Abstract Stability constants of the ternary palladium(II) complexes of triamine 2,2′:6′,2″-terpyridine (terpy) and some amino acids, peptides, DNA constituents or thiols were determined at 25 °C and at constant 0.1 mol dm^{-3} ionic strength, adjusted using $NaNO_3$. The coordination sites are pH-dependent. The results show the formation of binuclear species, 210. The speciation diagrams of various complex species were evaluated as a function of pH. Good correlations were found between the stability constants of the complexes and basicity of ligands.

1. Introduction

Interactions between proteins and nucleic acids may be promoted by metal ions. The various ternary complexes of nucleic bases and amino acids or peptides can be used to mimic the binding properties of the side chain donor groups of nucleic acids and proteins. Various tridentate ligands including diethylenetriamine (dien) and dipeptides form stable mononuclear complexes with palladium(II) even at very acidic pH. These "three coordinated" palladium(II) complexes were already extensively used as ideal "monofunctional" metal ions for examining the binding properties of various monodentate organic ligands (Kim and Martin, 1984; Illner et al., 2007; Ménard et al., 1987; Sheldrick and Neumann, 1994; Wienken et al., 1993; Kiss et al., 1997). To gain a high selectivity for the metal ion accompanied by an increased stability of the resulting base pair, the use of polydentate ligands as nucleobase surrogates is highly desirable (Sugimori et al., 1993; Zimmermann et al., 2002; Zhang and Meggers, 2005; Watson et al., 2005). The kinetics and mechanism of complex-formation reactions of $[Pd(AEP)(H_2O)]^{2+}$, where AEP stands for 1-(2-aminoethyl)piperazine, with biologically relevant ligands were studied as a function of selected nucleophiles and pH (Soldatović et al., 2009). The use of terpy as a tridentate ligand is well known to form self-assembling structures in the presence of metal ions (Constable et al., 2005) and has already been used to assemble DNA triangles (Choi et al., 2004). In addition to the expected high stability of its metal complexes, its large aromatic surface should stabilize the

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nucleic acid even further due to intense π-stacking with neighbouring base pairs. On the other hand, the π-stacking proposes the necessity for a planar metal ion complex.

The crystal and molecular structure of [Pd(terpy)Cl]Cl·2H_2O (Intille et al., 1973) and [Pd(terpy)(2,6-$C1_2$pcyd)] [PF_6], where pcyd = phenylcyanamide, (Zhang et al., 1993) have been determined by single crystal X-ray diffraction techniques. The author studied Pd^{II} complexes with aliphatic diamine derivative (N–N) type complexes in aqueous solutions (Shoukry et al., 1999; Shehata et al., 2011, 2012a,b,c,d), with 2-(2-aminoethyl)pyridine (Shehata et al., 2009), with 2,2′-bipyridine (Shehata, 2001) and (N–S) type (Shehata et al., 2008) complexes with bioligands in aqueous solution. The present investigation describes the equilibria associated with the interaction of $[Pd(terpy)H_2O]^{2+}$, as tridentate (N–N–N) ligand, with amino acids, peptides, DNA constituents or thiols.

2. Experimental

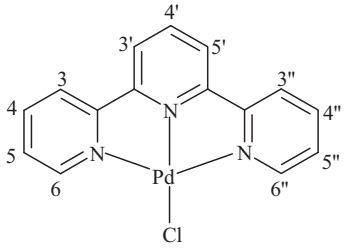
2.1. Materials

K_2PdCl_4, 2,2′:6′,2″-terpyridine, 4,4′-bipyridine, 2-mercaptoethanol, mercaptoacetic acid, 2-aminoethanethiol and methyl-thioglycolate were obtained from Aldrich. The amino acids and related compounds, glycine, alanine, β-alanine, valine, histidine, histamine dihydrochloride, ornithine, lysine, methionine and S-methylcysteine were provided by Sigma Chemical Co. Glycinamide, glycylglycine and asparagine were provided by BDH-Biochemicals Ltd., Poole, England. The DNA constituents, inosine, inosine-5′-monophosphate, guanosine-5′-monophosphate, cytidine, thymine, cytidine-5′-monophosphate, uracil, uridine and uridine-5′-monophosphate were provided by Sigma Chemical Co. For equilibrium studies, [Pd(terpy)Cl]Cl was converted into the diaquo complex by treating it with two moles of $AgNO_3$. The ligands in the form of hydrochlorides were converted into the corresponding hydronitrates by addition of appropriate amounts of $AgNO_3$. All solutions were prepared in deionised water.

2.2. Synthesis

[Pd(terpy)Cl]Cl·2H_2O was prepared by dissolving K_2PdCl_4, 2.82 mmol, in 10 cm^3 water. The clear solution of $[PdCl_4]^{2-}$ was filtered and 2,2′:6′,2″-terpyridine, 2.82 mmol, suspended in 10 cm^3 H_2O was added to the stirring solution. The pH was adjusted to 2-3 by the addition of HCl and/or NaOH. Yellowish-orange crystals of [Pd(terpy)Cl]Cl·2H_2O were formed and stirred for a further 30 min at 50 °C. After filtering off the precipitate, it was thoroughly washed with H_2O, ethanol and diethyl ether. Anal. Calcd. for $PdC_{15}H_{15}N_3O_2Cl_2$ (molecular weight = 446.6): C, 40.3; H, 3.4; N, 9.4%. Found: C, 40.2; H, 3.4; N, 9.5%.

^{1}H NMR, DMSO-d6, δ: 8.81, (2H, H3, H3″), 8.69, (2H, H6, H6″), 8.66, (2H, H3′, H5′), 8.61, (1H, H4′), 8.52, (2H, H4, H4″), 7.92, (2H, H5, H5″), are comparable with previous data (Müller et al., 2007).



2.3. Apparatus

Potentiometric titrations were performed with a Metrohm 686 titroprocessor equipped with a 665 Dosimat. The titroprocessor and electrode were calibrated with standard buffer solutions, prepared according to NBS specification (Bates, 1975). All titrations were carried out at 25.0 ± 0.1 °C in purified nitrogen atmosphere.

^{1}H NMR spectra were recorded on a Varian GEMINI 200 spectrometer at 200 MHz using TMS as an internal standard and d6-DMSO as solvent. The UV visible spectra were measured on a Shimadzu 3101 spectrophotometer.

2.4. Procedure and measuring technique

The acid dissociation constants of the ligands were determined by titrating 0.03 mmol (0.75 mmol dm^{-3}) samples of each with standard 0.05 mol dm^{-3} NaOH solutions. Ligands were converted into their protonated form with standard HNO_3 solutions. The acid dissociation constants of the coordinated water molecule in $[Pd(terpy)H_2O]^{2+}$ were determined by titrating 0.03 mmol (0.75 mmol dm^{-3}) of complex with standard 0.05 mol dm^{-3} NaOH solution. The formation constants of complexes were determined by titrating solution mixtures of the ligand, 0.03 mmol and $[Pd(terpy)H_2O]^{2+}$ in the concentration ratio of 1:1 and 1:2, ligand:Pd. The titrated solution mixtures each had a volume of 40 cm^3 and the titrations were carried out at 25 °C and 0.1 mol dm^{-3} ionic strength, adjusted with $NaNO_3$. A standard 0.05 mol dm^{-3} NaOH solution was used as titrant. The pH meter readings were converted to hydrogen ion concentration by titrating a standard HNO_3 solution, 0.01 mol dm^{-3}, the ionic strength of which was adjusted to 0.1 mol dm^{-3} with $NaNO_3$, and standard NaOH, 0.05 mol dm^{-3} at 25 °C. The pH was plotted against p[H]. The relationship pH − p[H] = 0.05 was observed.

The species formed were characterized by the general equilibrium

$$pM + qL + rH \rightleftharpoons (M)_p(L)_q(H)_r$$

for which the formation constants are given by

$$\beta_{pqr} = \frac{[(M)_p(L)_q(H)_r]}{[M]^p[L]^q[H]^r},$$

where M, L and H stand for [Pd(terpy)H2O]$^{2+}$ ion, ligand and proton, respectively. The calculations were performed using the computer program MINIQUAD-75 (Gans et al., 1976). The stoichiometry and stability constants of the complexes formed were determined by trying various possible composition

Table 1 Formation constants for complexes of $[Pd(terpy)(H_2O)]^{2+}$ with amino acids, thiols or 4,4′-bpy at 25 °C and 0.1 mol dm^{-3} ionic strength.

MLH[a]	$\log\beta$[b]			
	OH–	4,4′-bpy	Glycine	Valine
10-1	−5.52(3)	–	–	–
20-1	−1.07(4)	–	–	–
011	–	4.94(1)	9.61(1)	9.51(1)
012	–	8.39(1)	12.02(2)	11.82(2)
110	–	6.42(2)	8.06(2)	7.88(3)
111	–	9.12(3)	13.85(3)	13.77(4)
pK_a	–	2.70(4)	5.79(4)	5.89(5)
210	–	11.04(4)	12.31(3)	12.04(5)
$\log K_d$	4.45(5)	4.62(5)	4.25(4)	4.16(6)
	Alanine	β-alanine	S-Methyl-cysteine	Methionine
011	9.71(1)	10.11(1)	8.65(2)	9.12(1)
012	12.17(2)	13.75(2)	10.61(3)	11.39(3)
110	8.24(2)	8.48(3)	8.04(2)	8.16(2)
111	14.05(3)	14.40(4)	13.85(4)	13.97(4)
pK_a	5.81(4)	5.92(5)	5.81(5)	5.82(5)
210	12.53(5)	13.14(4)	14.18(6)	14.37(5)
$\log K_d$	4.29(7)	4.66(7)	6.14(8)	6.21(7)
	Histidine	Histamine	Ornithine	Lysine
011	9.15(1)	9.59(1)	10.58(2)	10.44(2)
012	15.30(2)	15.65(2)	19.43(2)	19.66(3)
013	17.00(3)	–	21.39(3)	21.78(3)
110	7.99(2)	7.81(4)	8.72(3)	8.53(3)
111	15.55(3)	15.45(2)	17.53(4)	18.04(4)
pK_a	7.56(4)	7.64(5)	8.81(5)	9.51(5)
210	13.50(6)	13.14(7)	14.76(6)	14.46(3)
$\log K_d$	5.51(7)	5.33(8)	6.04(7)	5.93(5)
	2-Mercapto-ethanol	2-Amino-ethanethiol	Mercapto-acetic acid	Methyl-thioglycolate
011	11.82(1)	10.69(1)	10.07(1)	7.89(1)
012	21.23(3)	18.87(2)	13.58(3)	–
110	9.42(4)	9.01(2)	8.79(3)	5.11(5)
111	18.37(5)	17.24(4)	16.01(3)	–
pK_a	8.95(9)	8.23(5)	7.22(5)	–
210	16.85(6)	16.30(5)	13.60(5)	–
$\log K_d$	7.43(7)	7.29(6)	4.81(6)	–

[a] M, L and H are the stoichiometric coefficients corresponding to Pd(terpy), ligand and H^+, respectively; the coefficient −1, refers to a proton loss; $\log K_d = \log\beta_{20\text{-}1} - \log\beta_{10\text{-}1}$ or $\log\beta_{210} - \log\beta_{110}$.

[b] Standard deviations in the last digit are given in parentheses; sum of square of residuals are less than 5×10^{-7}.

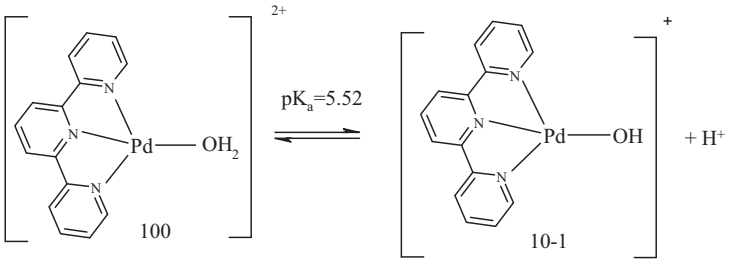
models for the systems studied. The model selected was that which gave the best statistical fit and was chemically consistent with the magnitudes of various residuals, as described elsewhere (Gans et al., 1976). Tables 1 and 2 list the stability constants together with their standard deviations derived from the MINIQUAD output. The concentration distribution diagrams were obtained with the program SPECIES (http://www.acadsoft.co.uk/scdbase/scdbase.htm, 1999) under the experimental condition used.

3. Results and discussion

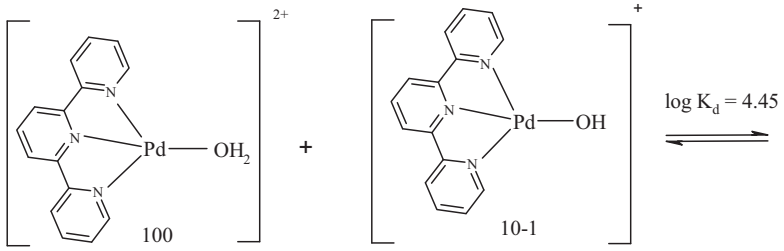
The acid dissociation constants of the ligands were determined under experimental conditions of 25 °C and constant 0.1 mol dm^{-3} ionic strength, adjusted with $NaNO_3$, which were also used for determining the stability constants of the Pd(II) complexes. The results obtained are in good agreement with the literature data (Kiss, 1990; Sóvágó, 1990;Lönnberg, 1990).

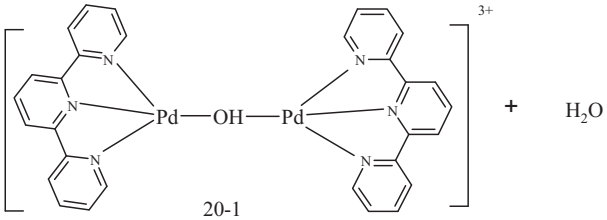
3.1. Acid-base equilibria of $[Pd(terpy)(H_2O)]^{2+}$

The best-fit model for the potentiometric data of $[Pd(terpy)(H_2O)]^{2+}$ was found to be consistent with two species: 10-1 and 20-1. The first one, 10-1 is due to deprotonation of the coordinated water molecule, as given in Eq. (1). The dimeric-μ-hydroxo complex, 20-1, is formed from the species 100 and 10-1 according to Eq. (2).



(1)





(2)

pK_a value for $[Pd(terpy)(H_2O)]^{2+}$ is 5.52. The equilibrium constant of the dimerization (see Eq. (2)) was calculated using the relationship: $\log K_d = \log \beta_{20\text{-}1} - \log \beta_{10\text{-}1}$ is 4.45.

The concentration distribution diagram for $[Pd(terpy)(H_2O)]^{2+}$ and its hydrolysed species are shown in Fig. 1A. The dimeric species, 20-1, predominates between pH ~4.2–6.8 with a maximum concentration of ~73% at pH 5.6. The monohydroxo species, 10-1 is the main species above pH ~6.8. The mono-aqua complex $[Pd(terpy)(H_2O)]^{2+}$, 100, is the main species up to pH ~4.2.

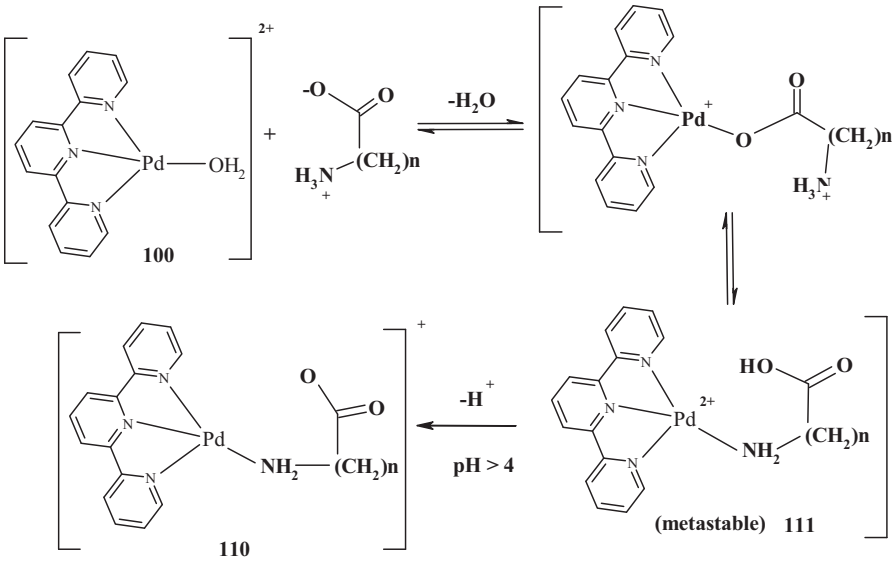
3.2. Complex-formation equilibria involving amino acids

The best-fit model for the potentiometric data of Pd(terpy)-amino acid system is found to be consistent with the unprotonated form 110, the protonated form 111 and the dimeric form 210, where one amino acid is coordinated with two palladium atoms through amino and carboxylate groups at the same time. The stability constants of $[Pd(terpy)(H_2O)]^{2+}$ with amino acids, $\log \beta_{110} \approx 7.88$–$8.72$ are found to be less than those of $[Pd(N\text{-}N)(H_2O)]^{2+}$, $\log \beta_{110} \approx 10$–$12$ (Shehata, 2001; Shoukry et al., 1999; Shehata et al., 2008, 2009, 2011). This was attributed to the fact that diamine complexes have two available sites for amino acid coordination through both the amino group and the carboxylate oxygen. However, in the case of $[Pd(terpy)(H_2O)]^{2+}$ it only has one site available for coordination, and amino acids may coordinate through the amino group or the carboxylate oxygen.

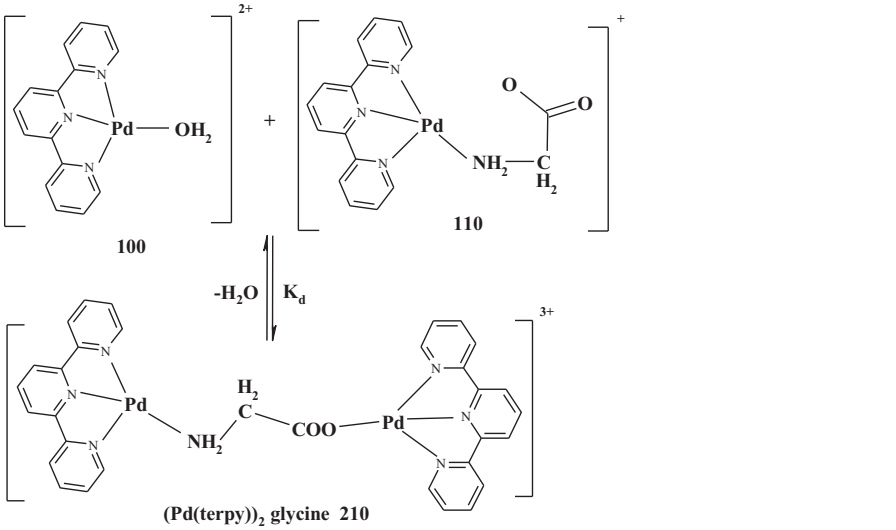
Multi-NMR studies (Appleton, 1997; Appleton et al., 1986, 1994) of complexes as $[Pt(NH_3)_3(H_2O)]^{2+}$, $[Pt(dien)(H_2O)]^{2+}$ and $[Pd(dien)(H_2O)]^{2+}$ with amino acids (aa) showed the initial formation of metastable isomer $[M(L)(Haa\text{-}O)]^{2+}$ at low pH, L = $(NH_3)_3$ or dien. These complexes were slowly converted to $[M(L)(Haa\text{-}N)]^{2+}$ isomer. Generally, the O-bound isomer is thermodynamically more stable for Pd(II) relative to Pt(II), reflecting some hardness of Pd(II) compared to Pt(II).

Similarly the amino acids coordinate with Pd(terpy) through the amino group NH_2 at high pH. At low pH the protonated species 111 is the main species, Fig. 1B–E, where both kinds of coordination such as $[Pd(N_3)Haa\text{-}O]^{2+}$ and $[Pd(N_3)Haa\text{-}N]^{2+}$ are involved with different proportions depending on the pH. At low pH the carboxylate oxygen is available for coordination leaving the amino group protonated. As the pH is increased the coordination site is shifted to the amino group, which is more favoured for Pd atoms. This is confirmed with the pK_a values of the protonated species 111, pK_a = 5.89 for $[Pd(terpy)\text{-}OCO\text{-}CH_2\text{-}NH_3]^{3+}$ which are larger than of those of COOH, 2.41 and smaller than those of the NH_3^+ group, 9.61. The pK_a values are acidified; less basic by coordination i.e. the pK_a values of the protonated complexes are lower than those of free uncoordinated ligands. The complex-formation equilibria may be represented in Eq. (3). The pK_a of the protonated complex was calculated from:

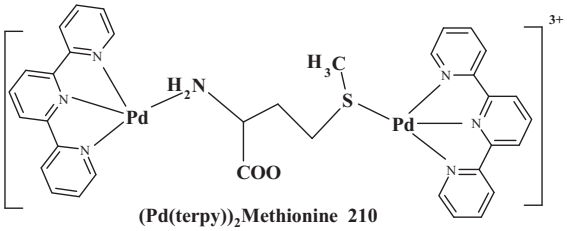
$$pK_a = \log \beta_{111} - \log \beta_{110}$$


100
-H2O
(CH2)n
H3N
Pd
O
HO
NH2
-H+
pH > 4
110
(metastable) 111

(3)


100
110
-H2O
Kd
NH2
C
H2
COO
(Pd(terpy))2 glycine 210

(4)


H3C
H2N
S
COO
(Pd(terpy))2Methionine 210

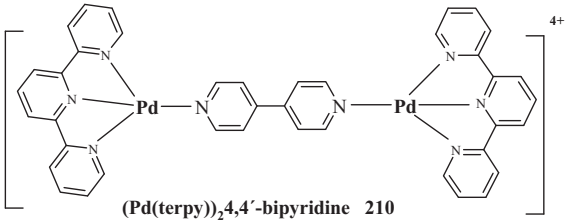

(Pd(terpy))2 4,4′-bipyridine 210

Table 2 Formation constants for complexes of $[Pd(terpy)(H_2O)]^{2+}$ with peptides and DNA units at 25 °C and 0.1 mol dm^{-3} ionic strength.

MLH[a]	$\log\beta$[b]		
	Glycineamide	Glycylglycine	Asparagine
011	7.88(1)	7.97(1)	8.56(1)
012	–	11.01(1)	10.79(2)
110	6.98(3)	7.07(2)	7.58(2)
111	13.12(3)	12.59(3)	13.32(7)
pK_a	6.14(4)	5.52(4)	5.74(7)
11-1	−1.99(3)	−1.16(3)	−0.87(2)
pK^H	8.97(4)	8.23(4)	8.45(3)
210	12.43(4)	12.31(4)	13.40(4)
$\log K_d$	5.45(5)	5.24(5)	5.82(5)
21-1	3.55(4)	4.46(5)	5.42(5)
pK^H	8.88(5)	7.85(6)	7.98(6)
	Inosine	Inosine-5′-monophosphate	Guanosine-5′-monophosphate
011	8.80(3)	9.02(2)	9.48(2)
012	–	15.24(3)	15.82(3)
110	7.52(3)	7.60(4)	7.85(4)
111	12.25(5)	13.73(4)	15.77(4)
pK_a	4.73(6)	6.13(6)	7.92(6)
112	–	18.27(8)	21.59(7)
pK_a	–	4.54(9)	5.82(8)
	Thymine	Uracil	Cytidine
011	9.65(1)	9.18(1)	4.23(3)
110	8.18(1)	8.15(1)	5.53(6)
	Cytidine-5′-monophosphate	Uridine	Uridine-5′-monophosphate
011	6.32(2)	9.01(1)	9.53(1)
012	10.82(3)	–	15.62(2)
110	6.68(4)	7.77(1)	8.09(2)
111	11.05(5)	–	14.94(2)
pK_a	4.37(7)	–	6.85(3)

[a] M, L and H are the stoichiometric coefficients corresponding to Pd(terpy), ligand, and H^+, respectively.; the coefficient −1, refers to a proton loss; $pK^H = \log\beta_{110} - \log\beta_{11\text{-}1}$; $\log K_d = \log\beta_{210} - \log\beta_{110}$ or $= \log\beta_{21\text{-}1} - \log\beta_{11\text{-}1}$.

[b] Standard deviations in the last digits are given in parentheses; sum of square of residuals are less than 5×10^{-7}.

According to Eq. (4), the dimerization constant of the dimeric species 210, $\log K_d$, can be calculated from the relation:

$$\log K_d = \log\beta_{210} - \log\beta_{110}$$

Concentration distribution diagrams for Pd(terpy) with glycine, alanine, β-alanine and methionine are given in Fig. 1B–E, respectively. The diagrams show the formation of the protonated species 111 at low pH. The dimeric species 210 is predominant in the pH range from ~4 to ~8. The unprotonated species 110 is the predominant species at higher pH up to pH ~10. The percentage concentration for the dimeric species, 210 follows the following order: methionine, ~81% at pH ~5.8 ≫ β-alanine, ~41% at pH ~5.8 > alanine, ~27% at pH ~5.8 > glycine, ~26% at pH ~5.8.

The very high percentage for methionine complex is attributed to the fact that methionine coordinates with two Pd atoms using N and S atoms but other amino acids coordinate using N and O atoms. Pd atoms favours S atoms more than O atoms. In case of β-alanine, alanine and glycine the trend follows the basicity of the amino acids.

The binuclear species (210) in case of 4,4′–bipyridine shows a higher concentration of ~70% at low pH ~2.8 and the mononuclear species, 110, is predominant between pH ~3.8 and 8.4, Fig. 1F.

3.3. Complex-formation equilibria involving thiols

Sulphur containing ligands react very easily with Pd(II) because of the great tendency of sulphur, soft Lewis base to form bonds with these metals, soft Lewis acids. The stability constants are correlated to the basicity of ligands, increase with the increase of ligand basicity. Stability constants are found to follow the order: 2-mercaptoethanol, (9.42) > 2-aminoethanethiol, (9.01) > mercaptoacetic acid, (8.79) > methionine, (8.16) > S-methylcysteine, (8.04) > methyl thioglycolate, (5.11).

Speciation diagrams of thiols show the formation of binuclear species (210) and the protonated species (111) at the physiological pH range, Fig. 2A and C, for 2-mercaptoethanol and 2-aminoethanethiol, respectively. For mercaptoacetic acid the

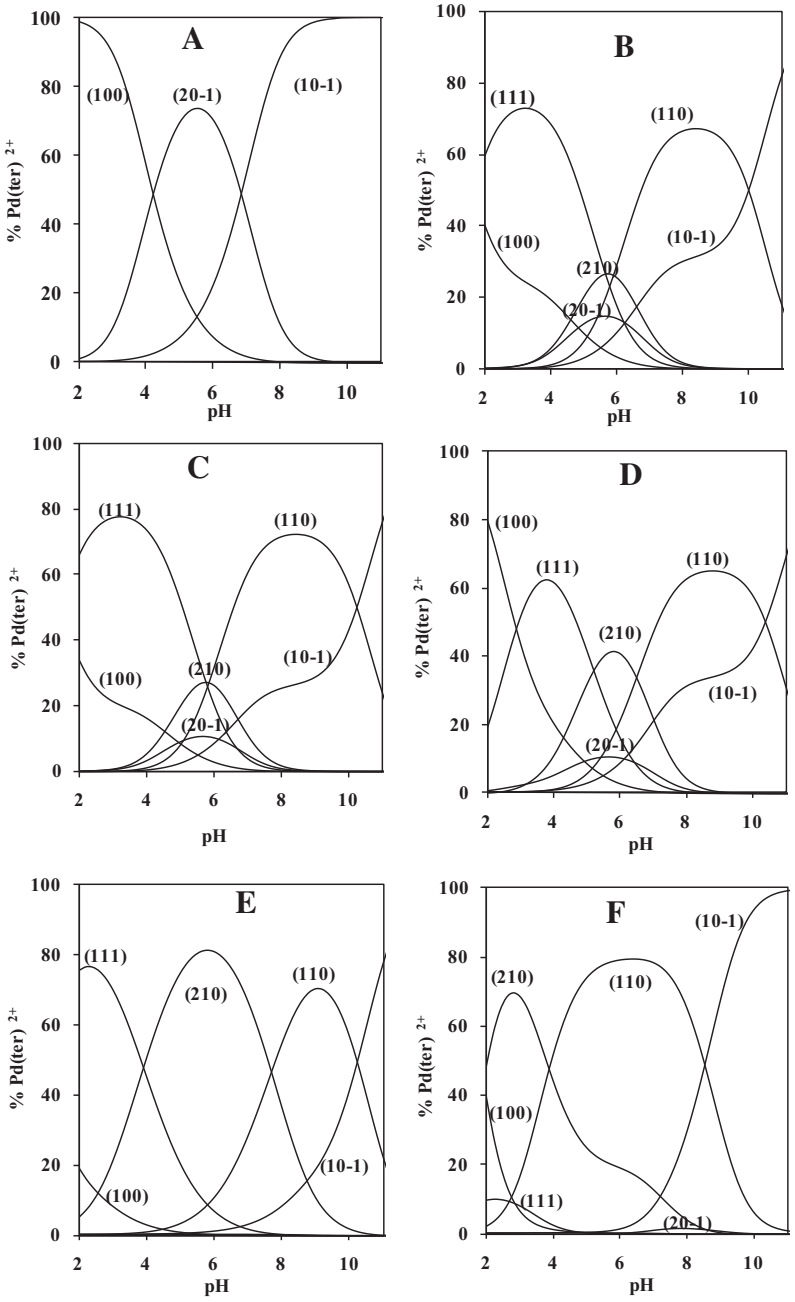


Figure 1 Concentration distribution of various species as a function of pH of $[Pd(terpy)(H_2O)]^{2+}$ with OH^-, (A) glycine, (B) alanine, (C) β-alanine, (D) methionine, (E) and 4,4′-bpy (F) (at concentration of 0.75 mmol dm^{-3} for $[Pd(terpy)(H_2O)]^{2+}$ and ligands).

protonated species (111) predominates at low pH up to pH ~7.2 and the species 110 above pH ~7.2, Fig. 2B. For methyl thioglycolate the species 110 has low percentage of 16.1% at pH 7.4, Fig. 2D.

3.4. Complex-formation equilibria involving peptides

The potentiometric data for peptide complexes were fitted on the basis of formation of complexes with stoichiometric coefficients 110, 111, 11-1, 210 and 21-1. In Fig. 3A for the complex with glycylglycine, which is taken as a representative of peptides, the protonated complex, 111 is formed at low pH with maximum concentration of 70% at pH ~3. The dimeric species, 210, is formed with a maximum concentration of 62% at pH ~5.5. At higher pH, the species 110, is formed with a maximum concentration of 56% at pH ~7.4. The species 21-1 has a smaller maximum concentration of 7.8% at pH ~8. At the pH higher than 8.42 the amide group undergoes deprotonation and the complex $[Pd(terpy)LH_{-1}]$, 11-1 is the main species. pK^H values of the amide groups incorporated in the Pd(II) complexes, $\log\beta_{110} - \log\beta_{11\text{-}1}$ are in the 3.85–8.64 range. The pK^H of the glutamine complex is markedly higher

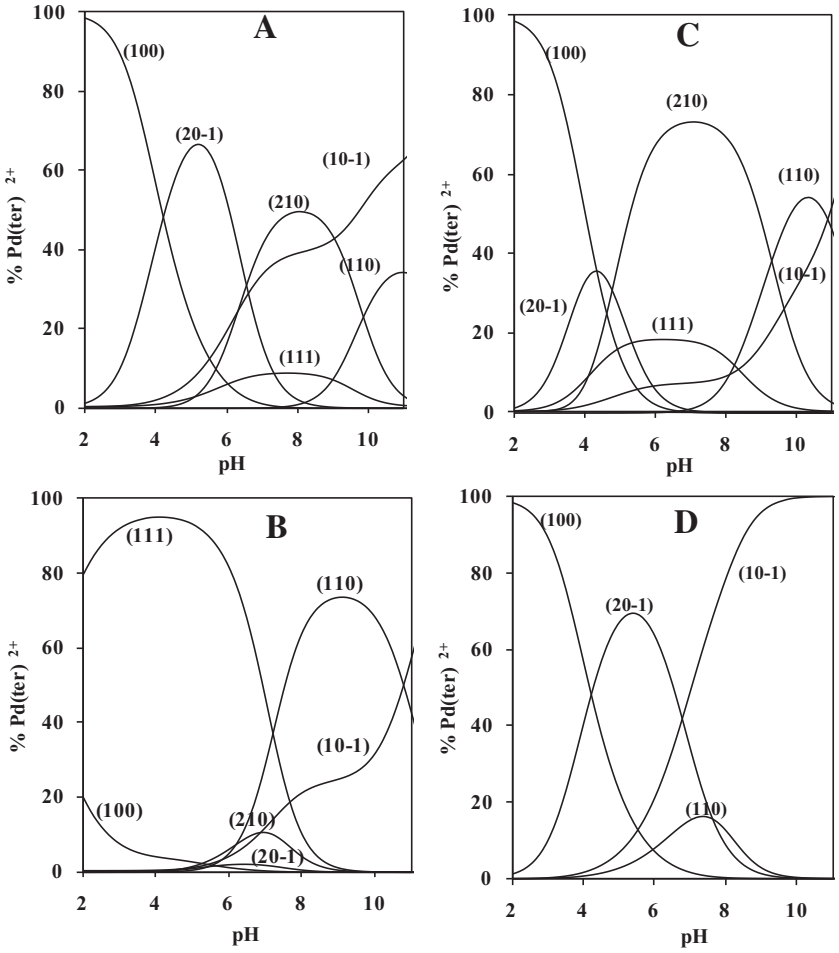


Figure 2 Concentration distribution of various species as a function of pH of $[Pd(terpy)(H_2O)]^{2+}$ with thiols: 2-mercaptoethanol (A), 2-aminoethanethiol (B), mercaptoacetic acid (C) and Methyl-thioglycolate (D) (at concentration of 0.75 mmol dm^{-3} for $[Pd(terpy)(H_2O)]^{2+}$ and ligands).

than those for peptide complexes, Table 2. This is ascribed to the formation of a seven-membered chelate ring, which would probably be more strained and therefore less favoured.

The relative magnitude of the pK^H values of the Pd(II) complexes with peptides has interesting biological implications. Under normal physiological conditions, pH 6-7 the peptide would coordinate with $[Pd(terpy)(H_2O)]^{2+}$ in entirely different fashions. Glutamate would exist solely in the protonated form, whereas other peptides would be present entirely in the deprotonated form. In addition, the slight difference in the side chain of peptides produces dramatic differences in their behaviour towards the palladium species.

3.5. Complex-formation equilibria involving DNA constituents

DNA constituents act as monodentate and form 1:1 complexes with $[Pd(terpy)(H_2O)]^{2+}$ ions. However, inosine, and nucleotides such as inosine-5′-monophosphate, guanosine-5′-monophosphate, cytidine-5′-monophosphate and uridine-5′-monophosphate form the monoprotonated complex, in addition to the formation of 1:1 complexes. Inosine-5′-monophosphate and guanosine-5′-monophosphate form in addition to the above species the diprotonated species 112. The pK_a value of the protonated inosine complex is 4.73. This value corresponds to N_1H. The lowering of this value with respect to that of free inosine, the pK_a = 8.80 is due to acidification upon complex formation. The pK_a values of the protonated nucleotide complexes are 6.13, 7.92, 4.37 and 6.85 for inosine-5′-monophosphate, guanosine-5′-monophosphate, cytidine-5′-monophosphate and uridine-5′-monophosphate complexes, respectively, Table 2.

3.6. Electronic spectra

The electronic spectra of $[Pd(terpy)(H_2O)]^{2+}$ in the absence (a) and presence of uracil (b), 2-Mercaptoethanol (c), Mercaptoacetic acid (d) and Methylthioglycolate (e) were performed in water. UV–visible spectrum of $[Pd(terpy)(H_2O)]^{2+}$, Fig. 4a, shows bands at 360, 343, 327, 313, 299sh, 276, 268, and 240 nm. UV–visible spectra of complexes b, c, d and e, show band shifts from those of $[Pd(terpy)(H_2O)]^{2+}$ which indicate the formation of the complexes, Fig. 4.

3.7. Stability-basicity correlations

The ability of ligands to bind to $[Pd(terpy)(H_2O)]^{2+}$ increases in most cases more or less linearly with increasing basicity of

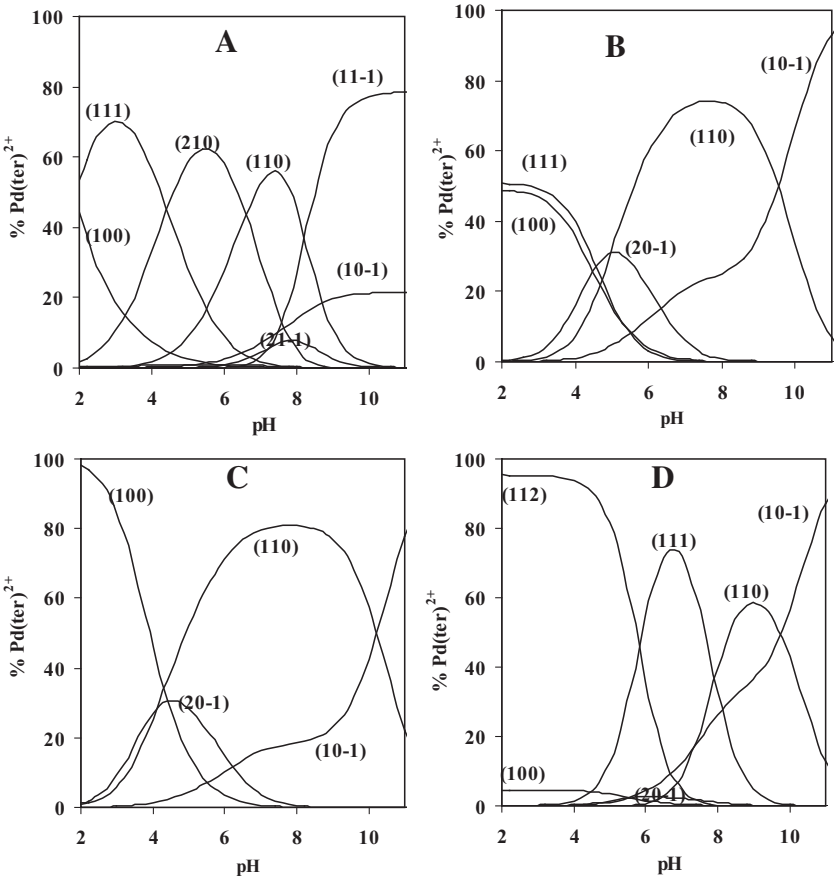


Figure 3 Concentration distribution of various species as a function of pH of $[Pd(terpy)(H_2O)]^{2+}$ with glycylglycine (A), inosine (B), uracil (C) and guanosine-5′-monophosphate (D) (at concentration of 0.75 mmol dm^{-3} for $[Pd(terpy)(H_2O)]^{2+}$ and ligands).

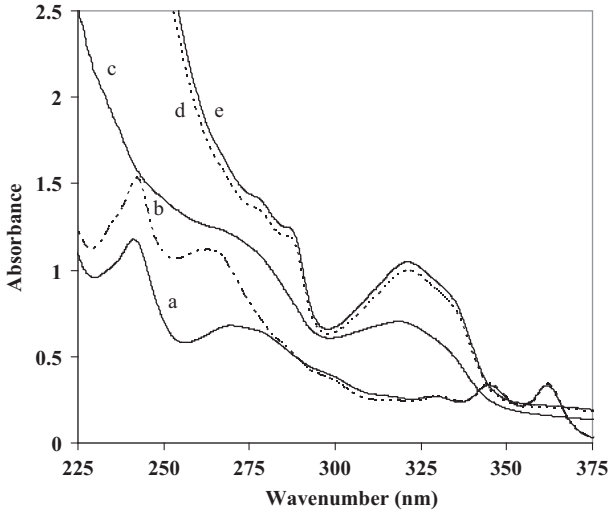


Figure 4 The electronic spectra of $[Pd(terpy)(H_2O)]^{2+}$ and its complexes: (a) 1 mmol dm^{-3} of $[Pd(terpy)(H_2O)]^{2+}$; mixtures (b), (c), (d) and (e) 1 mmol dm^{-3} of $[Pd(terpy)(H_2O)]^{2+}$ + 1 mmol dm^{-3} of NaOH + 1 mmol dm^{-3} of uracil, mercaptoethanol, mercaptoacetic acid or methylthioglycolate; respectively.

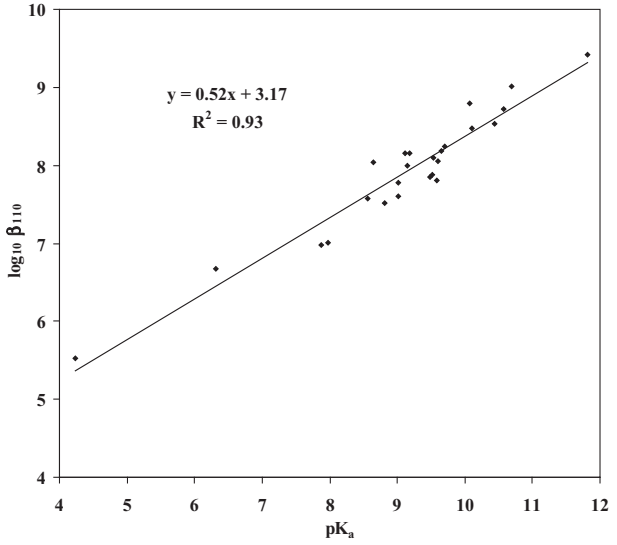


Figure 5 Correlation between Pd(terpy)-L stability and pK_a of more basic site of ligands.

ligands (Fig. 5). The deviation on linearity may be due to structural changes of the ligands.

4. Conclusion

The main goal of this research was to obtain stability constant data for $[Pd(terpy)(H_2O)]^{2+}$ complexes with amino acids, peptides, DNA constituents and thio-ligands. These data can be used to calculate the equilibrium distribution of $[Pd(terpy)]^{2+}$ species at different pH with variety of biologically important ligands in biological fluids. Ligands bind to $[Pd(terpy)]^{2+}$ in a monodentate fashion and it was found that their stability constants correlate in most cases more or less linearly with increasing basicity of ligands.

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